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Degradation of Congo red by integration of supported nanoscale zero-valent iron with photo-catalytic oxidation

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ABSTRACT

An integrated technology by coupling the attapulgite supported zero-valent iron nanoparticles (A-nZVI) with UV/H_2O_2 process was proposed for Congo red (CR) wastewater treatment. With the addition of 4.0 g/L A-nZVI, the removal efficiencies were found to be 86.38 and 53.98% for dye concentration and TOC in 10 min, respectively. For UV/H_2O_2 process alone, the TOC removal was merely 50.25% in 40 min. However, once UV/H_2O_2 process was integrated with A-nZVI, complete decolorization and mineralization of CR solution can be achieved, which indicated that the intermediate products of A-nZVI pretreatment were feasible to be mineralized by the following formed photo-fenton system.

Keywords: Nanoscale zero-valent iron; Photo-Fenton system; Azo dye; Decolorization; Mineralization

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1. Introduction

Azo dyes (–N=N– unit as the chromophore) were widely utilized in leather, paper-making, printing and textile dyeing because of their chemical stability and versatility [1]. These azo dyes are also known to be largely non-biodegradable in aerobic conditions and to be reduced to more hazardous intermediates in anaerobic conditions. Therefore, it is necessary to search for novel and efficient approaches to treat the industrial wastewater containing azo dyes. Up to now, the removal of azo dyes in wastewater mainly includes physical, chemical, biological methods or combination of various methods [2], such as electrochemical treatment [3], ozonation [4], photocatalysis [5], Fenton or Fenton like reagents [6], etc. Nevertheless, many of these methods are often ineffective for the destruction of azo dyes, and meanwhile result in a large quantities of solid waste or other environmental problems during the treatment processes [7].

Recently, a process based on zero-valent iron (ZVI) reduction for the degradation of organic compounds attracts much attention [8]. High decolorization rates were achieved in the reactions of nine azo dyes with particulate Fe° [9]. Compared with ZVI, nanoscale zero-valent iron (nZVI) possesses a larger specific surface area (SSA), higher reactivity and degrades many organic targets more effectively [10]. However, nZVI particles are easy to agglomerate into larger ones and are easy to be oxidized by non-target compounds because of the high surface energy and intrinsic magnetic interaction [11]. Several techniques have been designed for enhancing the stability of nZVI, such as supporting on solids [12] or entrapped in polymers [13]. Attapulgite, a crystalline hydrate magnesium silicate with a fibrous morphology, has been used for the framework of supporting nZVI in our previous research [14]. The nZVI reduction process was proved to be effective in decolorization, however it is limited in thoroughly mineralization [15], and a further treatment process, such as oxidation or biodegradation, is necessary to further mineralize the nZVI reduction effluent [16].

Advanced oxidation processes (AOPs), refer more specifically to a subset of such chemical processes that employ ozone (O_3), hydrogen peroxide (H_2O_2) and/or UV light, are widely utilized to successfully degrade organics

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in industrial wastewater and groundwater, which rely on in-situ production of highly reactive hydroxyl radicals ·OH [17]. Although UV/H_2O_2 process often performed great efficiency both on decolorization and mineralization, UV light efficiency is always lower in wastewater treatment due to the high absorbance by dye molecular [15]. Thus, an integrated technique using Fe° and UV/H_2O_2 sequential photo-catalytical oxidation for complete decolorization and mineralization of dye compounds was well demonstrated by the research group under instruction of Shu [15,18]. Based on our previous work, nZVI supported on attapulgite (A-nZVI) was firstly introduced into the integrated process for the degradation of azo dye Congo red (CR). The operating parameters such as the dosage of A-nZVI and H_2O_2, reaction time, and solution pH value were investigated based on the removal efficiencies of dye and total organic carbon (TOC). Moreover, a modified pseudo-first order kinetic equation was developed to calculate the kinetic rates.

2. Materials and methods

2.1. Materials

Congo red (CR) was purchased from the Development Center of Kemiou Chemical Reagent without further purification, the basic characteristics was list in Table 1, and the chemical structure was shown in Fig. 1. Hydrogen peroxide was bought from Sinopharm Chemical Reagent Co. Ltd (30%, w/w). A-nZVI was prepared using a conventional liquid-phase method as reported in our previous research [14]. The nZVI was well dispersed on the surface of acid-treated attapulgite with no obvious aggregation of the nanoparticles. The content of nanoscale zero valent iron was determined to be 3.50%, according to the procedure proposed by Gu et al. [19].

2.2. Degradation process

All the batch experiments for the removal of CR in aqueous solutions were performed in 500 mL glass bottles. For A-nZVI reduction decolorization, 250 mL 100 mg/L of CR solutions were mixed with the accurately weighted A-nZVI (1.0, 2.0 and 4.0 g/L), which was immediately sealed and then put in a vapor-bathing at a constant temperature of 25 ± 0.5°C and vibrated at a speed of 200 rpm for 120 min. At defined time intervals, 5.0 mL of the solution were withdrawn and filtrated for further analysis.

Table 1
The basic characteristics of Congo Red

Medical subject headings	Congo Red
CAS registry number	573 – 58 – 0
IUPAC name	Disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl) diazenylphenyl]phenyl] diazenyl-naphthalene-1-sulfonate
Chemical formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Molar mass	696.665
λ_{max} (nm) in pH 7.3 aqueous solution	488
Molar attenuation coefficient (L mol^{-1} cm^{-1})	45000

In the UV/H_2O_2 process, the photodegradation of CR was carried out in a XPA-7 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China), and the 300 W medium pressure mercury lamp was selected as the light sources throughout the experiment. Then, the quartz tubes with 50 mL 60 mg/L or 100 mg/L CR solution and certain concentration of H_2O_2 were put in the photochemical reactor and stirred with magnetic stirrers. Then, an aliquot of solution was sampled at regular intervals to be analyzed the absorbance (wavelength at 488 nm), total organic carbon (TOC), color strength of dye solution referencing of the American Dye Manufactures Institue (ADMI) and the pH value.

For experiments integrating A-nZVI reduction with UV/H_2O_2 process, A-nZVI particles were initially added and mixed with the original dye solution reaction for 10 min. After A-nZVI decolorization, the treated dye wastewater was withdrawn and separated with A-nZVI particles by a filter then transferred to the UV/H_2O_2 process for further treatment.

2.3. Analysis

The pH value of samples was adjusted to 7.3 by using diluted NaOH and HCl. Then, all the samples were detected at 488 nm of maximum absorbance wavelength by T60 UV-VIS Spectrophotometer (Beijing Purkinje General Instrument Co. Ltd). TOC was determined with multi N/C 2100 (Analytik jena AG,Germany). Furthermore, ADMI was measured by HACH DR/4000U UV-Vis Spectrophotometer. The iron concentration was identified using TAS-990 Atomic Absorption Spectrophotometer (Beijing Purkinje General Instrument Co., Ltd). The value of pH was measured on a pH meter (pHS-3B, Shanghai, China).

2.4. Removal kinetics

A pseudo-first order reaction model was used for the study of CR removal kinetic characteristics under UV/H_2O_2 process, which followed the equation [18],

$$\frac{dC_{CR}}{dt} = k_{obs} C_{CR} \tag{1}$$

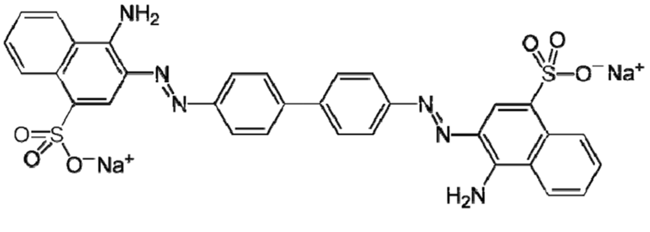

Fig. 1. Chemical structure of CR.

$$\frac{C_{CR}}{C_{CR-0}} = e^{-k_{obs}t} \tag{2}$$

where k_{obs} is a pseudo-first order kinetic constant, C_{CR} represents the concentration of CR, C_{CR-0} is the CR initial concentration, t is time.

As for A-nZVI reduction process, the reaction always occurs in the non-homogenous water–iron interphase, which relys on the dosage of iron addition. A modified pesudo-first order kinetics (Eq. (3)) was proposed by as following [18],

$$\frac{C_{CR}}{C_{CR-0}} = \frac{C_{CR-0} - C_{res}}{C_{CR-0}} \times e^{-k_{obs}t} + \frac{C_{res}}{C_{CR-0}} \tag{3}$$

And the removal efficiency of CR ($R\%$) under A-nZVI reduction can be calculated as

$$R\% = \frac{C_{CR-0} - C_{res}}{C_{CR-0}} \times \left(1 - e^{-k_{obs}t}\right) \tag{4}$$

where C_{res} is the ultimate residual CR concentration after A-nZVI addition [18].

All experimental tests were conducted in triplicate while blank samples with no A-NZVI addition were served as control. Excel 2010 and Origin 8.5 analysis software for windows were used for the simulation of removal kinetics.

3. Results and discussion

3.1. Reductive decolorization of CR by A-nZVI

The nZVI particle addition in aqueous phase has proved to be a fairly fast successful process to reduce azo dyes resulting from the azo link cleavage in the dye molecule by electrons transfering [20], and the decolorization efficiency is affected by the solution pH value especially in alkaline region due to the precipitation of ferrous hydroxide on the surface to occupy the reactive sites [21]. Under A-nZVI reductive decolorization, the dye concentration, ADMI and TOC of CR solution with time courses were shown in Fig. 2a. With the addition of 4.0 g/L A-nZVI particle, the effective removal efficiencies were found to be 86.38 and 91.31% for dye concentration decreasing from 100 to 13.62 mg/L and ADMI reducing from 29058 to 2526 after 10 min, respectively. Go by 30 min, the removal efficiencies of CR concentration and ADMI were exceed in 90%. As for TOC removal, it was dropped to its maxium 53.98% at first 10 min and then slowly rebound by time extension due to the release of adsorbed TOC in the surface of A-nZVI. It can be inferred that, in A-nZVI reduction process, the chromophore –N=N– of azo dye is cleaved resulting dye concentration and ADMI drop, though much less reduction for TOC. Moreover, the removal efficiencie of TOC was apparently higher than reported [18], it may be attributed to the A-nZVI with huge specific surface area and less agglomeration.

The variations of the pH and iron concentration in the process of reaction were shown in Fig. 2b. Iron concentration was found to be increased slowly from none initially to 0.62 mg/L in first 30 min and then maximum 0.69 mg/L at 60 min, significanly lower than iron powder or unsupported nZVI reduction process [18]. Additionally, pH changed from original 7.44 to 9.67 in 2 min and then keepping about 9.65.

The CR dye removal efficiency was depended on A-nZVI dosage addition and the results are illustrated in Fig. 3a. The dye removal efficiency enhanced significantly from 75.89%, 87.51% to 91.63% by elevating the dosage of A-nZVI to 1.0, 2.0 and 4.0 g/L. It was obvious that more A-nZVI dosage addition obtained the more removal efficiency, which indicated that more iron surface active sites for collision with dye molecules resluting in speeding up the initial reaction. As pointed out in the previous work on the reductive decolorization of diazo dye CI Acid Black 24 by zero-valent iron powder, color removal efficiencies were found to be improved with the increasing dosage of iron particles [15]. TOC removal efficiency also rising from 32.76, 48.87 to 53.98% at 30 min with the increasing A-nZVI dosages (Fig. 3b).

As indicated in Fig. 3a, it have goodness-of-fit by comparing the regression lines of modified pesudo-first order

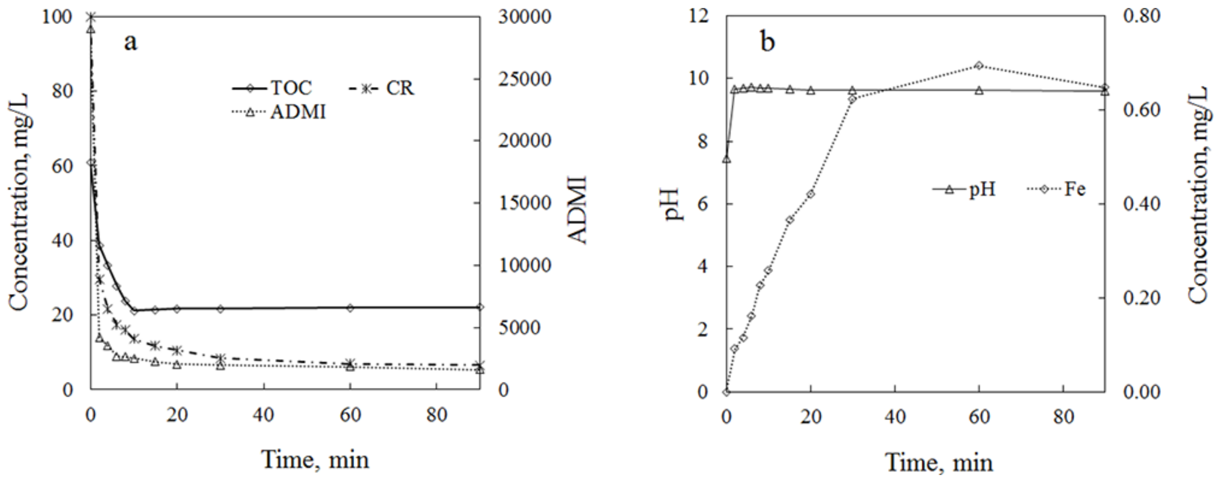

Fig. 2. The dye concentration, TOC, and ADMI color index (a) and pH value, iron concentration (b) of CR wastewater versus time under A-nZVI reductive decolorization. C_{CR-0} = 100.0 mg/L, A-nZVI dosage = 4.0 g/L.

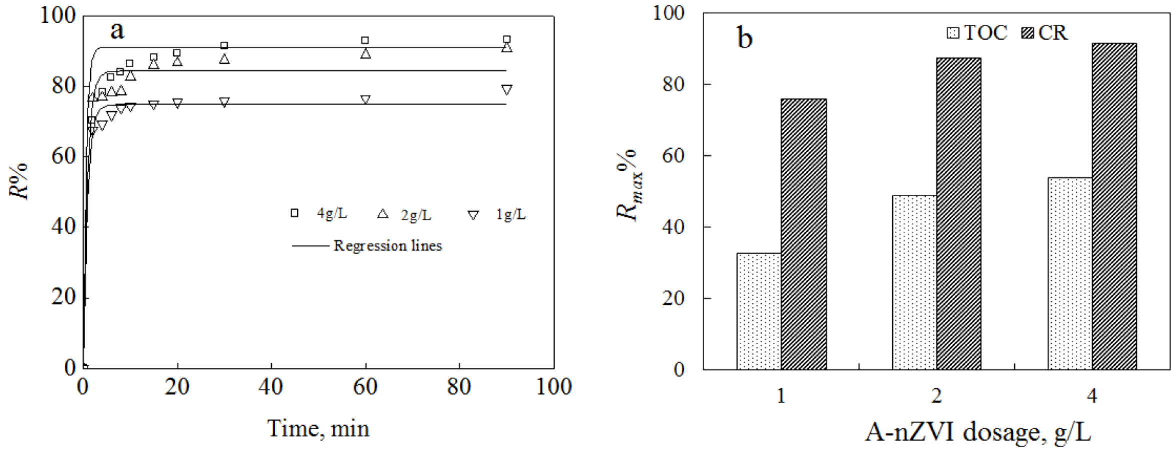

Fig. 3. Effect of A-nZVI dosages on the removal of CR and TOC under A-nZVI reductive decolorization, (a) simulation of CR removal by modified pesudo-first order kinetics, (b) removal rates of CR and TOC at 30 min. C_{CR-0} = 100.0 mg/L.

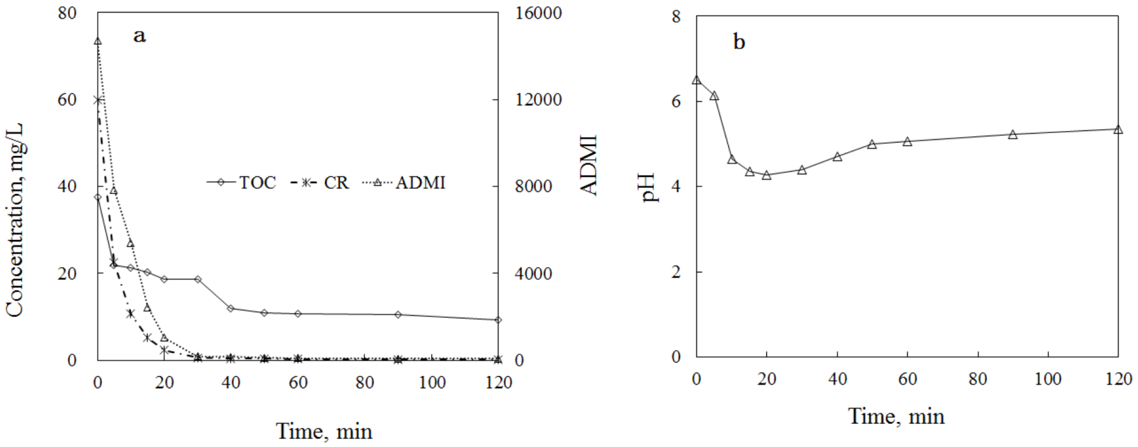

Fig. 4. The dye concentration, TOC, and ADMI color index (a) and pH value (b) of CR wastewater versus time under UV/H_2O_2 degradation. C_{CR-0} = 60.0 mg/L, $C_{H_2O_2}$-0 = 19.8 mmol/L, 300 W of medium pressure mercury lamp.

kinetics with experimental data with the R^2 values of 0.9961, 0.9664 and 0.9873 for A-nZVI dosages of 4.0, 2.0 and 1.0 g/L, respectively. The ultimate residual dye concentration declined significantly and the reaction rate improved fastly with the increasing A-nZVI dosage. According to the simulation, 24.50, 12.20 and 7.52 mg/L of C_{res}, 1.0905, 1.0932 and 1.71043 min^{-1} of rate constant k_{obs} were acquired at A-nZVI dosages of 1.0, 2.0 and 4.0 g/L, repectively. The rate constants were comparatively higher than that of Shu et al. [19], which were between 0.0604 and 0.02236 min^{-1} for 100 mg/L of Acid Black 24 by adding 0.0335 to 0.1674 g/L of iron.

3.2. Photo-catalytical oxidation process

In the UV/H_2O_2 process, organic compounds in the solution was degradated by UV light at a certain wavelength originated from pressure mercury lamp light, and the operating conditions should be optimum, such as initial concentration of dye or hydrogen peroxide and pH. As shown in Fig. 4a, 60 mg/L CR with the addition of 19.8 mmol of H_2O_2, after irradiation about 40 min, the dye concentration and ADMI color unit decreased rapidly, but TOC concentration decreased less. Actually, the high removal efficiencies can be acquired over 98.0% for CR concentration and ADMI, these two reduced from 60 to 0.6 mg/L and from 14,736 to 192 about 30 min. TOC removal was merely 50.25% during the same time period and slowly approaching 70.52% at the 120 min. Moreover, the pH of variation tendency was gently, the original pH of 6.52 declined to 4.27 and increased gradually to 5.35 (Fig. 4b).

Many researchers [22–24] have revealed that the successful degradation of dye solutions in UV/H_2O_2 process was depended on higher initial H_2O_2 concentrations, it can generate a non-selective and powerful oxidant, ·OH radicals under the condition of direct photolysis ($H_2O_2 + hv \rightarrow 2 \cdot OH$). In this research, with the addition of H_2O_2 in the range of 1.1 to 19.8 mmol, higher removal efficiency was obtained for the degradation of CR (Fig. 5a). The color removal efficiency was only 28.3% in direct UV irradiation alone without hydrogen peroxide over 20 min and the acquisition of the observed first order rate constant by Eq. (2) was about 0.03386 min^{-1}. But in the same time, the removal efficiencies were increased clearly to 73.3 to 96.1% by adding 1.1~19.8 mmol of hydrogen peroxide. With the increase of time, higher removal efficiencies of CR was achieved (99.3%). The effects of hydrogen peroxide concentration on TOC removal and pseudo-first order kinetic constant k_{obs} after 120 min of reaction are demonstrated in Fig. 5b, and 19.8 mmol of hydrogen peroxide concentration was served as the optimum in the following experiments. The k_{obs} value proportionately increased from 0.03386 to 0.08714, 0.11149, 0.14012, 0.1664, 0.18763 min^{-1} by adding hydrogen peroxide concentration from 0 to 1.1, 6.6, 9.9, 13.2, 19.8 mmol. Similar result was reported in literature [18], but other reports also observed that the concentration of H_2O_2 may either enhance or inhibit the photoreaction rate depending on concentration.

3.3. Integration of A-nZVI reduction with UV/H_2O_2 oxidation process for degradation CR solution

As demonstrated above, UV/H_2O_2 oxidation process performed effectively for not only color removal but also TOC removal (at high 70.52%), although the latter demanded longer time (120 min). On the other hand, the high decolorization efficiencies were obtained but low TOC removal (only 53.98%) in A-nZVI reduction process. In order to prompt the mineralization of azo dye moleculars, an integrating process of A-nZVI reduction and UV/H_2O_2 oxidation was conducted for the treatment of CR solution.

The removal of dye color and TOC by the proposed integration process was shown in Fig. 6. 90.38% and 50.42% of dye and TOC removal were obtained in 10 min after adding 4.0 g/L A-nZVI, but more than 99.60% and 92.65% were achieved in following 110 min by UV/H_2O_2 process (19.8 mmol of H_2O_2). Moreover, the iron ions concentration in solution rose from 0 to 0.58 mg/L in first 10 min of A-nZVI reduction, then increased little during UV/H_2O_2 oxidation.

The effect of A-nZVI dosage on the removal of both color and TOC is also shown in Fig. 7a and Fig. 7b. For the demanding time of 90% of dye decolorization, 45 min was needed for UV/H_2O_2 alone. With 10 min of pre-reduction treatment, only 42, 25 and 2 min was further needed by UV/H_2O_2 process at the dosage of 1.0, 2.0 and 4.0 g/L. So, the combination process should be a feasible attempt in organic wastewater treatment in saving time and energy. As for TOC removal, the integrated technique acquired 79.42, 81.09 and 92.65% of removal rates within summation time of 120 min at the A-nZVI dosage of 1.0, 2.0 and 4.0 g/L, higher than sole A-nZVI reduction (53.98% at 4.0 g/L) and UV/H_2O_2 alone (70.52% at 19.8 mmol). In mechanism, electrophilic attack is usually the first step in oxidation, organic compounds with pronounced electron withdrawing characters (such as $-NO_2$, –Cl and –N=N– groups) are always resistant be mineralized through oxidative pathways but are subject to initial reductive transformation [25]. Moreo-

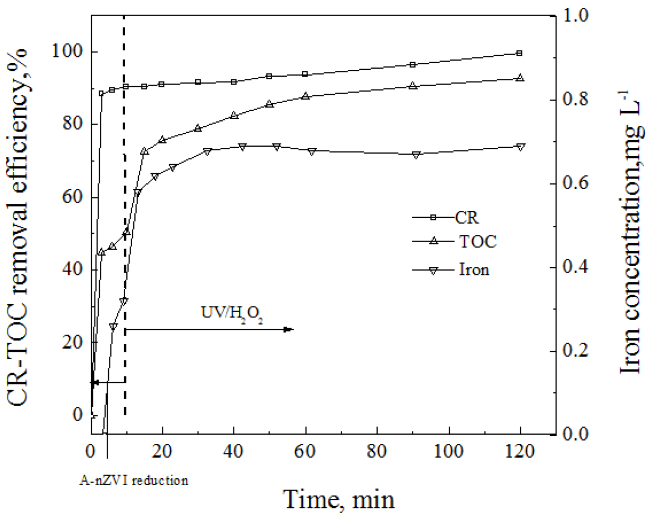

Fig. 6. Decolorization, TOC removal and iron concenration various in the integration process of initially 10 min of A-nZVI reduction and the following 110 min of UV/H_2O_2. A-nZVI dosage = 4.0 g/L, $C_{H_2O_2\text{-}0}$ = 19.8 mmol/L, 300 W of medium pressure mercury lamp.

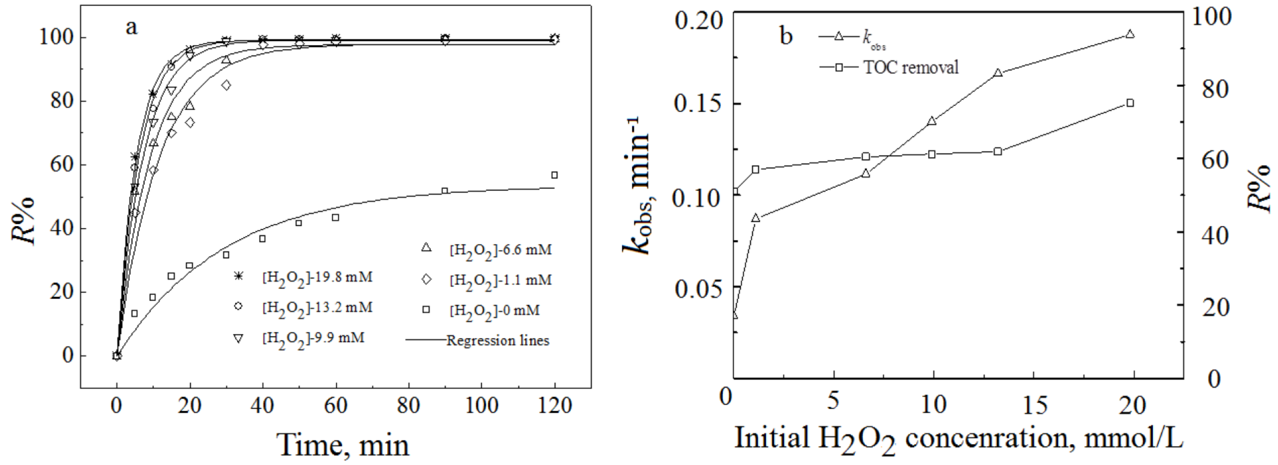

Fig. 5. Effect of H_2O_2 concentrations on the removal of CR, TOC and pseudo-first order kinetic constant K_{obs} under UV/H_2O_2 process, (a) simulation of CR removal by modified pesudo-first order kinetics, (b) TOC and K_{obs}·C_{CR-0} = 60.0 mg/L, H_2O_2 concentrations varied in 0–19.8 mmol/L.

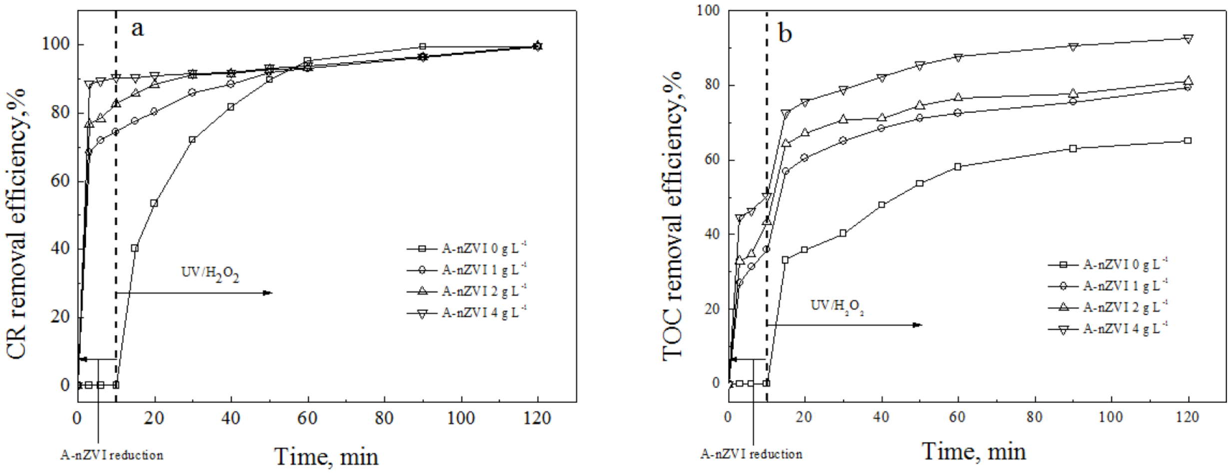

Fig. 7. Effects of A-nZVI dosage on decolorization and TOC removal in the integration process of initially 10 min of A-nZVI reduction and the following 110 min of UV/H$_2$O$_2$·C$_{H2O2-0}$ = 19.8 mmol/L, 300 W of medium pressure mercury lamp.

ver, afterwards the dye solution was separated with A-nZVI particles, soluable or complexed Fe^{2+} is still left in the dye solution. With the following UV/H$_2$O$_2$ process, a photo-fenton system was formed, H$_2$O$_2$ decomposes catalytically by means of Fe^{2+}, giving rise to hydroxyl radicals (Fe^{2+} + H$_2$O$_2$ + $hv \rightarrow$ Fe^{3+} + ·OH + OH$^-$).

4. Conclusions

The CR wastewater was easy to be decolorized by A-nZVI reduction (4.0 g/L) or UV/H$_2$O$_2$ oxidation (19.8 mmol/L) process, and the efficiency were both found to be over 90% in 30 min. But during the same time period, the mineralization rate for TOC were only ~50% when them used alone, although 70.52% of TOC removal by UV/H$_2$O$_2$ oxidation was achieved as the treatment time reached 120 min in total. However, once UV/H$_2$O$_2$ process was connected together with A-nZVI reduction, complete decolorization and 92.65% of mineralization of dye bath effluent can be achieved. The intermediate products of A-nZVI were feasible to be mineralized by the following formed photo-fenton system, and the integrated technique is promising and thus has bright prospects for the treatment of azo dyes.

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